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Anomaly of Specific Heat in α-Phase Alloys of Copper and Aluminium*

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Synopsis

The specific heats of 12 copper alloys containing less than 14.59 per cent of aluminium were measured at high temperatures at annealed and baked states by the inverse rate curve method. In the case of the α-phase alloy containing more than 3.98 per cent of aluminium, the specific heat-temperature curve shows, in an annealed state, a small maximum at the temperature about 340 to 300°; the temperature lowers with the increase of aluminium content and the anomaly is most conspicuous in the alloys containing 8.05 or 9.14 per cent of aluminium. The anomaly is also observable in alloys in the mixture range; in the specific heat curve of these alloys, another maximum is observed at about 400°, the origin of which was uncertain. When the alloys are heated at 210° for 200 hours, the anomaly in the α-phase becomes very large, and the temperature of the maximum is almost constant (about 305°). The anomaly observed at high temperature is considered to be caused by the formation of a superlattice of short range order Cu_3Al.

I. Introduction

It is well known that the physical and mechanical properties of α-aluminium bronze are remarkably influenced by cold-working; for example, the alloy, when heated after cold-working, shows an anomalous increase in tensile strength(1) and a decrease in electric resistance(2) at about 250°, whereas an alloy containing 9 per cent of aluminium shows an anomaly in the electric resistance at about 300°(3) after annealed at high temperatures.

Various explanations(4) have hitherto been given on the cause of such an anomaly shown in α-aluminium bronze; recently, Dr. S. Yamada(2) suggested the possibility of the existence of a superlattice in the system of copper and aluminium, which might be considered as the origin of the anomaly, though no evidence was yet obtained.

In the present investigation, the specific heat was systematically measured at high temperatures with 12 kinds of annealed alloys in α-solid solution and $\alpha + \delta$ mixture range and the existence of a superlattice was ascertained.

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* The 813th report of the Research Institute for Iron, Steel and Other Metals.
Read at the meetings, April 3 and Sept. 24, 1950 and April 1, 1952 of the Japan Institute of Metals and published in the Journal of the Institute (Nippon Kinzoku Gakkai-Si), **18** (1954), 98.

(1) S. Yamada, Nippon Kinzoku Gakkai-Si, **5** (1941), 390.

(2) T. Matsuda, Sci. Rep., Tôhoku Imp. Univ., **14** (1925), 343; S. Yamada, loc. cit.; Nippon Kinzoku Gakkai-Si, **6** (1942), 169.

(3) I. Obinata, Mem. Ryojun Coll. Eng., **2** (1929), 205.

(4) K. Honda, Kinzoku no Kenkyû, **3** (1926), 1; G. Masing, Z. Metallkde., **16** (1926), 301; T. Kawai, Kinzoku no Kenkyû, **10** (1933), 302; S. Yamada, loc. cit.

II. Specimens and method of measurement

The specimens were prepared from electrolytic copper and aluminium, the chemical analyses of which are given in Table 1. In preparing the specimen, the above metals were melted in a coke furnace and cast into a square iron mould 25 mm in side length, then forged and lathed to a cylinder 18 mm in diameter and 38 mm in length, and finally along its central axis, a hole 3 mm in diameter and 17 mm in depth was drilled at both ends. The results of chemical analysis of aluminium contained in the specimens are given in Table 2.

Table 1. Results of chemical analysis of the metals.

Metal	Fe (%)	Si (%)	Cu (%)	Zn (%)	C (%)	As (%)	Sb (%)	S (%)	Ni (%)	Pb (%)	Bi (%)	Ag (%)	Mn (%)	P (%)
Electrolytic Cu	0.00_1	—	—	0.01_6	—	0.01_0	0.00_6	0.01_6	0.00_2	0.01_1	0.00_2	0.00_2	—	—
Al	0.14	0.42	0.00_5	0.04	0.00_0	—	—	0.00_1	—	—	—	—	trace	none

Table 2. Results of chemical analysis of the alloys.

No. of specimen	1	2	3	4	5	6	7	8	9	10	11	12
Al (%)	3.13	3.98	5.15	6.16	6.83	8.05	9.14	10.35	11.27	12.74	13.43	14.59

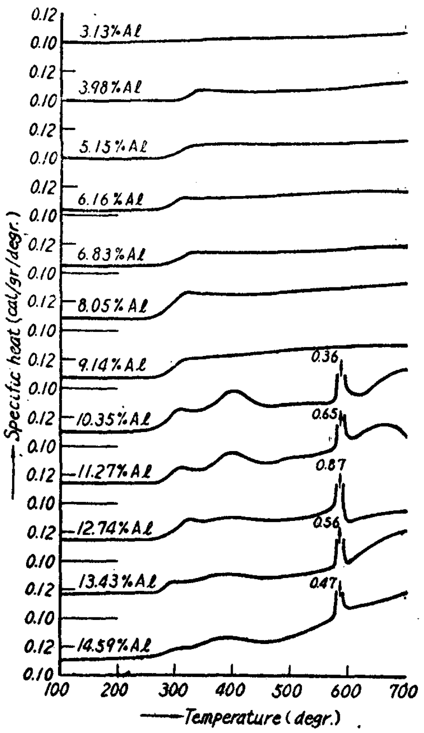

Fig. 1. Specific heat curves of the annealed Cu-Al alloys.

The specimens were all annealed in vacuum at 700° for 1 hour and then cooled down to room temperature at the rate of 30° per hour. Further, in order to develop the anomalies, the specimens were heated at 210° for 200 hours after annealing and cooled down to room temperature at the same rate as the above.

The measurement was carried out in vacuum with the apparatus used previously in the investigation on α-phase alloys of copper and zinc system(5), and as a standard specimen, pure copper was used, the values obtained by F. Wüst(6) being adapted in the calculation of specific heat.

III. The results of measurement

The results of measurement of the specific heat of the annealed alloys in the α-phase and the $\alpha+\delta$-phase of copper and aluminium are shown in Fig. 1. As shown in this figure, no

(5) H. Masumoto, H. Saitô, M. Sugihara, Nippon Kinzoku Gakkai-Si, **16** (1952), 359; Sci. Rep. RITU, **A4** (1952), 481.

(6) F. Wüst, Int. Crit. Tables, **5**, 93.

anomaly is observable in the alloys containing less than 3.13 per cent of aluminium, but the alloy containing 3.98 per cent of aluminium clearly shows a small maximum at the temperature ranging from 300 to 350°. The maximum becomes conspicuous and the temperature lowers with the addition of aluminium. The maximum also appears in the specific heat curve of an alloy in the mixture range containing more than 10.35 per cent of aluminium (see the phase diagram Fig. 2), and the temperature slightly lowers with the increase of aluminium content, the maximum becoming inconspicuous. Further, in the curves of these mixture range alloys, two other maxima are observed, one being at about 585° which might be due to the latent heat by the eutectic transformation, $\alpha+\delta\rightarrow\beta$, and the other being at about 400° and becoming smaller with increasing aluminium content; the reason for the appearance of this maximum can not still be explained.

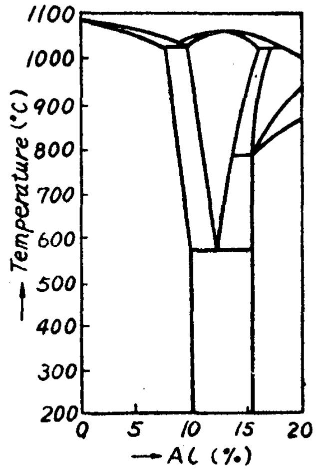

Fig. 2. Phase diagram of Cu-Al system.

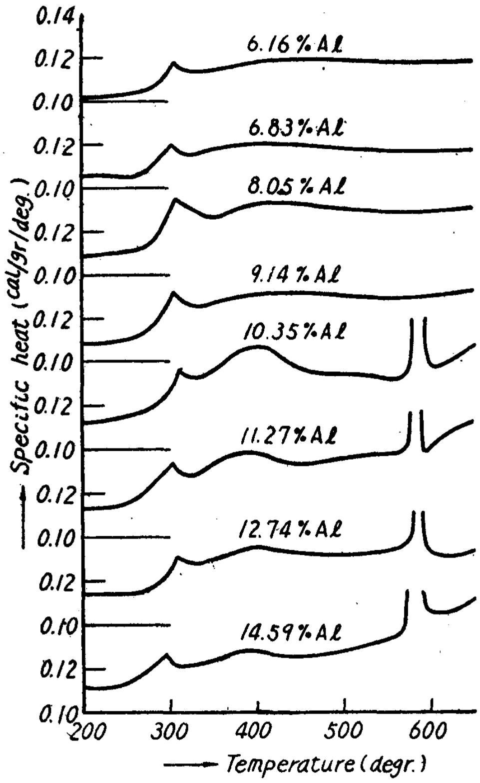

Fig. 3. Specific heat curves of the Cu-Al alloys baked at 210° for 200 hours.

The results of the measurement with the alloys cooled slowly down to room temperature after the heating at 210° for 200 hours are shown in Fig. 3. Compared these results with those shown in Fig. 1, it will be clear that after the above treatment, the maximum at about 300~350° becomes large showing a tail ranging to about 600° and that the temperatures of the maximum slightly lower to about 305°, being almost constant in all alloys.

Dr. I. Tarora[7] reported that the specific heat curves of the alloy in β phase did not show any anomaly when the alloy was perfectly decomposed into α and δ phase by heating them at 550° for 10 hours after the annealing. To examine this point, in the present investigation, the measurement was also made with the alloys in β phase which were cooled slowly to 550° after the annealing mentioned above and heated for 3.5 and 10 hours; but, no other result than that shown in Fig. 1 was obtained. This discrepancy may be explained as follows: In Dr. Tarora's

(7) I. Tarora, Nippon Kinzoku Gakkai-Si, 8 (1944), 143.

exepriment, the thermal analysis was made by the method of differential cooling curve with the alloy containing 7 per cent of aluminium and the rest of copper as a neutral material, which resulted in the cancellation of the two anomalies occurring at almost the same temperature in the specimen and the neutral meterial.

It can be seen from the above results that in the α-phase alloys of copper and aluminium, a remarkable rearrangement of the constituent atoms takes place at about 200~350°, the degree of which is influenced by heat treatment, and that the rearrangement becomes remarkable with the aluminium content. What is first considered may probably be the existence of a superlattice transformation, Cu_3Al. According to a consideration on the forms of the specific heat curve and of the electric resistance-temperature curve(3), this superlattice may be in a short range ordered state. The composition of Cu_3Al, however, can not be realised in α-phase which contains 12 wt.-per cent of aluminium, as δ-phase begins to appear at the concentration of about 9 per cent of aluminium.

Thus, it can be concluded that the occurrence of the anomaly in the α-phase alloys of copper and aluminium is due probably to the existence of the superlattice, Cu_3Al.

Summary

By measuring the specific heats at high temperatures of the alloys in the α-phase and mixture range of copper and aluminium system, subjected to various kinds of heat treatments, the following results were obtained.

(1) The specific heat curves of the α-phase alloys containing more than 3.98 per cent of aluminium which were slowly cooled from 700° shows a small maximum in the range from 300 to 350°, showing an anomaly in the α-phase. This anomaly becomes conspicuous and the temperature lowers with the increase of aluminium content. In the case of the alloys in the mixture range, the same anomaly, which becomes smaller with the increase of aluminium content, and another uninterpretable maximum at about 400° are observed.

(2) When the alloys were heated at 210° for 200 hours after the annealing, the maximum mentioned above becomes large and the temperature is almost constant (about 305°) in all the alloys.

(3) The transformation of the superlattice Cu_3Al in short range ordered state was suggested at high temperatures in α-phase alloys.

In conclusion, the present investigators wish to express their hearty thanks to Messrs. M. Sugihara, Y. Sugai and M. Shinozaki for the trouble they have taken in carrying out this investigation.